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Optimization and application of the gas-diffusion flow injection method for the determination of chloride

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A selective and sensitive procedure for the fast and indirect determination of chloride by the gas-diffusion FIA method has been optimized and applied for the determination of chloride in water samples which contained different amounts of the analyte. The examined samples were: seawater, tap water and very pure water from the water-steam system of the power plant "Nikola Tesla B" in Obrenovac. Application of an amperometric detector (model LC-17A; BAS, West Lafayette, USA) enables the detection limit to be decreased down to 0.05 μmol/dm^3 of chloride, which corresponds to 35.5 pg, and adjustment of the acceptor flow rate and direction inside the gas-diffusion unit. In this way the optimized FIA system has excellent repeatability. For 5 μmol/dm^3 it was found to be 1.11 % ($n = 5$). The throughput of this method is 60 samples per hour.

Keywords: gas-diffusion flow injection method, amperometric detection, indirect chloride determination.

INTRODUCTION

Neutral chlorine does not exist in nature. As a result of its extreme positive redox potential and electronegativity, chlorine occurs only as chloride. It can be found in large amounts in seawater, as well as in sediments bound to cations such as potassium and sodium. Chlorine can be used as a disinfectant, a water purifier or as a bleaching agent. It is obvious that the determination of chloride is important. Tracking its concentration shows the level of water pollution. Therefore, it is not surprising that a number of flow injection (FI) methods have been developed for this analyte.[1–7]

The quality of water in power plant systems is important, especially for turbine maintenance. Turbines are very sensitive to the presence of corrosive substances such as NaOH, NaCl, Na_2SO_4, organic and inorganic acids, iron and copper oxides, because they cause the oxidative burst of metal under pressure. The maximum allowed concentration[8] of chloride is 10 μg/dm^3. Deviation from the allowed concentration causes pitting corrosion and corrosion strain. Pitting corrosion occurs if:

1. There is increased tension within the material;
2. A material sensitive to this kind of corrosion is being used (Cr-Ni steels);
3. Impurities that cause this corrosion are present ($Cl^–$, $OH^–$).

Increased concentration of chloride in the system water-steam occurs because of:

1. Breakthrough of cooling water in the condenser;
2. Poorly performed chemical preparation;
3. The use of inappropriate cleansing agents for blades during maintenance.

Standard methods for tracking the level of chloride in the system are spectrophotometry and ion-chromatography. The spectrophotometric metod is based on the reaction of chloride with mercury(II) thiocyanate.[9] The method is used for the concentration range of 5 ppb to 1 ppm. Chloride reacts with mercury(II) thiocyanate forming thiocyanate ion, which forms the red coloured iron(III) thiocyanate complex. Interferences are caused by bromide, iodide, thiosulphate, hydrazine and nitrites. Ion chromatography[9] is used for the concentration range of 1 to 3 ppb. Strong acids and bases cause interference. The presence of boric acid can cause deformation of the peaks.

EXPERIMENTAL

Reagents and materials

All the chemicals used were of analytical-reagent grade. The aqueous reagent and standard solutions were stored in polyethylene bottles. Deionized water was used throughout. A saturated solution of $KMnO_4$ served as the oxidizing agent. It was prepared by boiling the saturated solution with subsequent filtering in order to remove MnO_2 and any excess of $KMnO_4$ that might be present. A stock solution of 0.1 mol/dm^3 NaCl was prepared from BDH (Poole, Dorset, UK) concentrated volumetric standards, which are certified to have an accuracy within the factor limits of 0.999 and 1.001. Standard Cl^- solutions, which, in most of the experiments were made in 3 mol/dm^3 H_2SO_4, were prepared by diluting aliquots of the stock solution to the appropriate volumes. Solutions of I^-, Br^- and BrO_3^- were prepared by dissolving appropriate amounts of KI (Jugolek, Beograd, Yugoslavia), KBr and $KBrO_3$ (Zorka, Šabac, Yugoslavia).

Instrumentation and apparatus

The FIA manifold used for the determination of chloride is illustrated in Fig. 1. Two peristaltic pumps were used. One was a Model HPB 5400 (Iskra, Kranj, Slovenia), and the other one was a Moled MS REGLO (Ismatec, Zürich, Switzerland). The injection valve was a Model 5020 (Rheodyne, Cotati, CA, USA) equipped with a 200 µl sample loop. The gas-diffusion unit was obtained from the Shenyang Film-Projector Factory (Shenyang, China). The PTF membrane that separates the donor and acceptor stream does not need to be changed for experiments, which last for less than 10 hours. All concentrations were made with 0.5 mm i.d. tubing.

The flow-through amperometric cell LC-17A (BAS, West Lafayette, USA), shown in Fig. 2, consists of a platinum working electrode and counter electrodes. The working electrode has two separate electrodes embedded in a Kel-F block. The entire block easily withstands exposure to the solvents and temperatures. The reference electrode is an Ag-AgCl with a 3 M NaCl gel filling solution (all electrode potentials refer to this reference electrode). The auxiliary electrode is a solid stainless steel block. A gasket defining the flow channel is sandwiched between the auxiliary and the working electrode block. The platinum-working electrode was polished occasionally in a specific manner. First, it was rinsed with water followed by methanol, then it was polished with alumina polish slurry, rinsed with distilled water and acetone and finally air dried. The potential to the flow-through

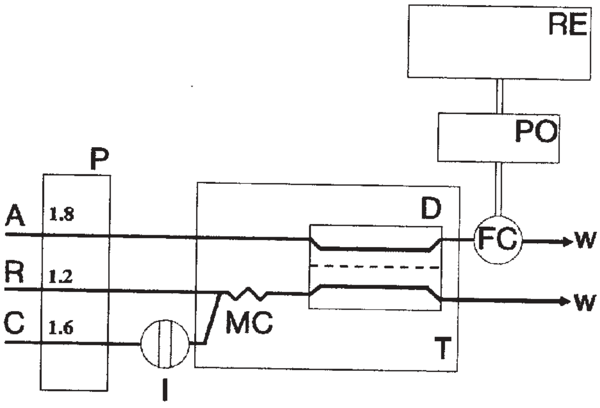

Fig. 1. FI manifold used for the indirect determination of chloride: A – acceptor solution (0.01 mol dm^{-3} H_2SO_4); R – reagent (saturated $KMnO_4$); C – carrier (3 mol dm^{-3} H_2SO_4); P – peristaltic pump; I – injection valve; MC – mixing coil; D – diffusion cell; FC – electrochemical flow-through cell; PO – potentiostat; RE – recorder and W – waste.

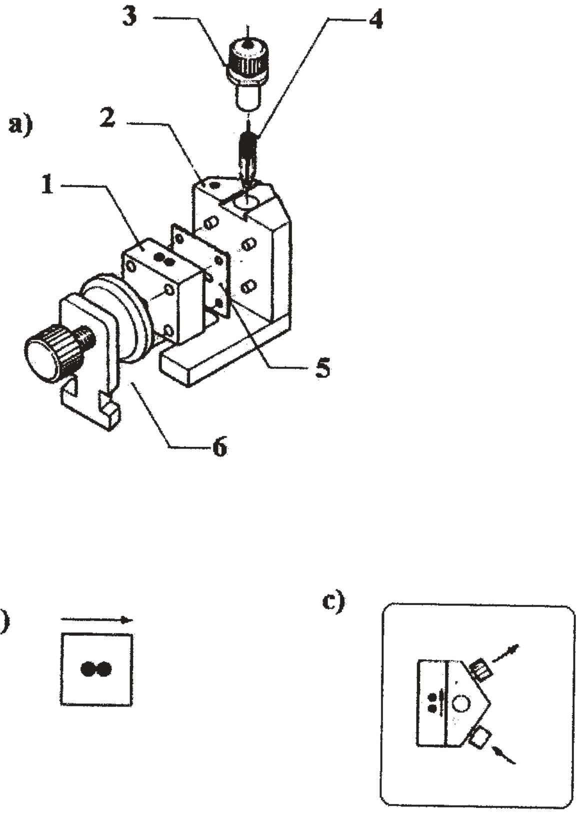

Fig. 2. The flow through the amperometric cell: a) 1 – working electrode block; 2 – auxiliary electrode; 3 – locking collar; 4 – miniature reference electrode; 5 – gasket; 6 – quick release mechanism; b) working platinum electrode geometry; c) top view.

amperometric cell was applied and currents were measured with a Model MA5450 polarograph (Iskra, Kranj, Slovenia); the resulting FI signals were recorded on a Model 61 Servograph (Radiometer, Copenhagen, Denmark) strip-chart recorder. Temperature regulation was achieved with a constant-temperature bath, type Messgeraete-Werk Lauda, Germany.

The chloride solution, which was injected by the injection valve, is carried by the carrier stream (sulphuric acid solution) and reaches the mixing coil where it is mixed with the reagent (saturated potassium permanganate solution) and oxidized to chlorine. The chlorine diffuses through the micro porous membrane in the gas-diffusion unit from the donor into the acceptor stream. The other products of the reaction exit the system as waste. Chlorine, taken by the acceptor stream, reaches the amperometric cell where it is reduced to chloride. The recorder registers the cathode current, which is proportional to the concentration of chloride in the sample.

RESULTS AND DISCUSSION

The effects of several parameters on the performance of the flow injection system were studied.

The effect of the potential applied at the working platinum electrode was investigated in the range of +0.20 to +0.70 V *versus* the Ag-AgCl reference electrode. The hydrodynamic voltammogram for a 2.50 mmol/dm^3 sodium chloride standard in 3 mol/dm^3 sulphuric acid is shown in Fig. 3. As can be seen, the optimum potential is +0.30 V.

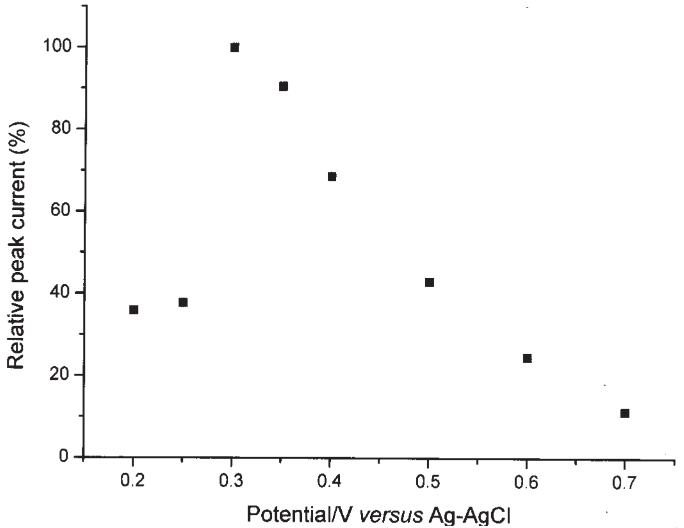

Fig. 3. Hydrodynamic voltammogram for a 0.200 cm^3 injection of a 2.50 mmol/dm^3 sodium chloride standard.

The effect of sulphuric acid concentration on the peak currents was studied by injecting the same chloride standard (2.50 mmol/dm^3) but with the concentration of the acid varying between 1.0 to 5.0 mol/dm^3. From the obtained data, it can be seen that the current increases exponentially with increasing H_2SO_4 concentration. A simple equation of the type: $I = 1.50 \exp(0.84c)$ (where I is the current in μA, and c is the concentration of H_2SO_4 in mol/dm^3) fits the data very well. The corresponding correlation coefficient was found to be 0.9954.

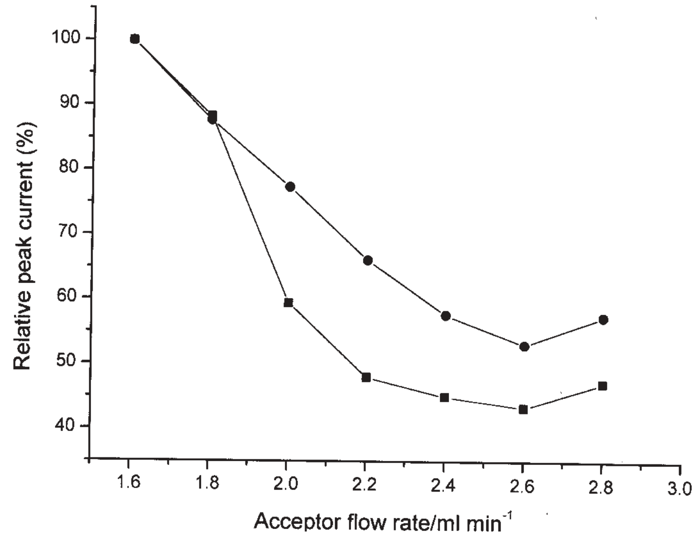

Fig. 4. Acceptor flow rate and direction effect (the circles present parallel flow while the squares present counter flow).

A 0.01 mol/dm^3 H_2SO_4 solution was used as an acceptor.[10]

The effect of the acceptor flow rate and flow direction was investigated in the range of 1.6 to 3.0 ml/min. The donor flow rate was constant (2.8 ml/min). The data obtained are shown in Fig. 4. As can be seen, the optimal flow rate was 1.8 ml/min for a parallel flow direction of both the acceptor and the donor stream. It was previously determined that an *n* times decrease of the acceptor flow rate results in an *n* times increase of the FIA signal.[11]

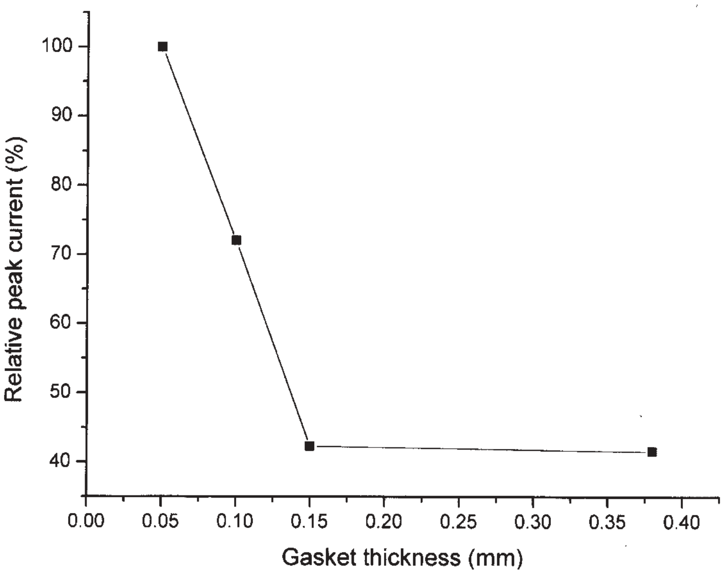

Fig. 5. Effect of the gasket thickness.

The effect of the gasket thickness was studied, as this is an important factor that determines the working solution volume. The results of the study of this effect are presented in Fig. 5. As it can be seen the 0.05 mm thick gasket gave the best result and was used throughout.

The effect of temperature was examined by injecting a 2.50 mmol/dm^3 NaCl standard in a 3 mol/dm^3 H_2SO_4 solution, while varying the temperature in the interval 20 – 60 ºC. The obtained data show that there is an exponential dependence described by the function $I = 2.67 \exp(0.06t)$ (where I is the current in µA, and t is the temperature in ºC). The correlation coefficient was 0.9986. This finding is interesting, as a change in temperature not only affects the oxidation rate, but also the solubility of the formed chlorine, the diffusion process and the reduction of chlorine at the platinum working electrode. However, due to the amperometric cell properties, stable signals are obtained even at low temperatures.

The detection limit determined by a recommended procedure[12] at room temperature and a 3 mol/dm^3 H_2SO_4 solution as the carrier was 0.05 µmol/dm^3, which corresponds to 35.5 pg of chloride (the sample loop volume was 200 µl). The throughput of this method was 60 samples per hour.

The determination of chloride by this technique can be interfered with by ions that can be oxidized by potassium permanganate to form neutral molecules, if the neutral molecules have a relatively high vapour pressure and a low water solubility so that they can diffuse through the PTF membrane into the acceptor stream and if the molecules that get into the acceptor stream are electroactive at the working potential.

These conditions are fulfilled by iodide, bromide and hydrazine (present in the power plant water samples).

To inhibit the 24.44 % increase of FIA signal caused by the presence of bromide, the procedure decribed in the work of Kubala[13] was used. This iodate pre-treatment method is based on the classical argentimetric procedure:

$$IO_3^- + 6Br^- + 6H^+ \rightarrow I^- + 3Br_2 + 3H_2O$$

The formed bromine is expelled from the solution by heating for 15 min on the water bath. Iodide does not interfere.

Applying this pre-treatment method enables the determination of chloride in the presence of bromide whose concentration is 1 µg/dm^3 with an insignificant increase of the FI signal, compared to the signal of pure chloride standard. The difference is then –3.84 % (1 mmol/dm^3) and –3.46 % (0.5 mmol/dm^3). The interference of hydrazine (1 µg/dm^3) was eliminated by adding 0.5 µmol/dm^3 bromate and heating on a water bath for 15 min.

The reproducibility of the method is shown in Fig. 6. The relative standard deviation for a 2.00 mmol/dm^3 chloride solution was found to be 0.61 % ($n = 5$) whereas for a 5.00 µmol/dm^3 solution it was 1.11 % ($n = 5$).

This method was used for the determination of chloride in seawater, tap water, commercial mineral water and water taken from the water-steam system of the power plant "Nikola Tesla B" in Obrenovac.

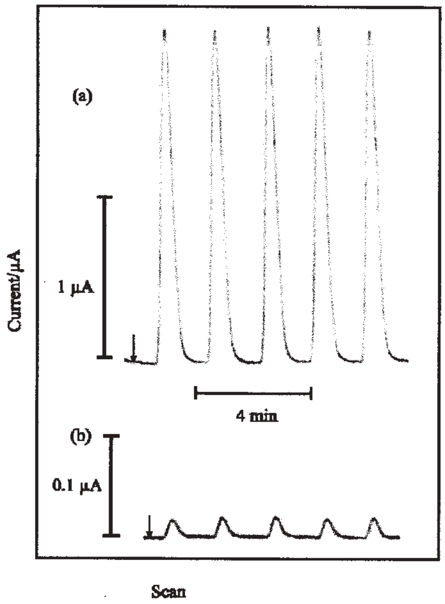

Fig. 6. Response of the amperometric detector to: (a) five repetitive injections of a 2.00 mmol/dm^3 chloride standard; and (b) five repetitive injections of a 5.0 µmol/dm^3 chloride standard.

Two calibration runs were screened, one for samples containing higher chloride concentrations (seawater) and the other one for lower concentrations. The first one was obtained by injecting in triplicate a total of five chloride standards between 10 and 100 mmol/dm^3 in 3 mol/dm^3 sulphuric acid (the 0.5 mm thick gasket was used). The sulphuric acid aided the expulsion of carbonates from the samples. The linear regression equation was $I = (8.143 \pm 0.576)c + (0.709 \pm 0.036)$ (I is the peak current in µA, and c is the concentration of Cl$^-$ in mmol/dm^3), with a correlation coefficient of 0.9926. The second one was made for tap water, mineral water and water samples from the power plant. This one was obtained by injecting in triplicate a total of six chloride standards between 5 and 100 µmol/dm^3 in 3 mol/dm^3 sulphuric acid (the 0.05 mm thick gasket was used here). The linear regression equation was $I = (0.0028 \pm 0.0001)^c + (0.014 \pm 0.007)$ (I is the peak current in µA, and c is the concentration of Cl$^-$ in µmol/dm^3), with a correlation coefficient of 0.9961.

Two procedures were introduced for the pre-treatment of the power plant samples because of the possible presence of hydrazine. Under the given conditions, hydrazine is oxidized by permanganate to form nitrogen, which can diffuse through the PTF membrane. Adding 0.5 µmol/dm^3 KBrO$_3$ and heating the mixture for 15 min on a water bath was one procedure and the other one was the standard complement method (the standard complements were 5, 10 and 15 µmol/dm^3 of chloride standard). Both methods showed good agreement with a difference of less than 1 %.

The results obtained for all examined samples are shown in Table I. The seawater samples were taken from the Tivat bay, Montenegro. Obtained results show that the samples Župa and Krasići, taken further away from the coast, have a higher concentration of chloride than the Kaliman sample. There are several reasons that can explain this. The first one is that there are several springs of non-salty water located near the coast and the second is that the outlets of the local sewage pipes are located further away from the coast, and as it is known that sewage contains certain amounts of chloride, the obtained results are acceptable.

TABLE I. Results of the chloride determination in the examined water samples

Sample		concentration		
		Argentimetric	FI	Label
Minakva (commercial mineral water)			15.7± 0.2 mg/dm^3	17.35 mg/dm^3
Mivela (commercial mineral water)		21.73± 0.04 mg/dm^3	21.05± 0.03 mg/dm^3	17 mg/dm^3
Belgrade tap water			13.32± 0.05 µg/dm^3	
			10.37±0.07 µg/dm^3	
		12.61± 0.05 µg/dm^3	12.24±0.05 µg/dm^3	
Water from the power plant	I		1.41± 0.06 µg/dm^3	
	II		0.85± 0.03 µg/dm^3	
	III		< 0.355 µg/dm^3	
Seawater	Kaliman		4620± 6 mg/dm^3	
	Zupa		9940±8 mg/dm^3	
	Krasići	10500±5 mg/dm^3	10230±8 mg/dm^3	

The samples from the power plant represent condensed purified water before it is brought onto the turbines. The previously determined conductivities of these samples were 0.25 µS (I), 0.18 µS (II) and 0.08 µS (III). It can be concluded that there are some other substances other than chloride that affect the conductivity, most probably silicates.

CONCLUSIONS

A rapid, indirect gas-diffusion flow injection method with amperometric detection has been developed for the selective determination of chloride. The method is based on the oxidation of chloride to chlorine by a saturated potassium permanganate solution. The chlorine diffuses through the micro-porous membrane in a gas-diffusion unit from the donor into the acceptor stream, and is amperometrically quantified on a platinum working electrode.

The effect of the following variables on the performance of the system was studied:

1. The potential of the working Pt electrode (+0.30 V *vs.*Ag/AgCl was chosen);
2. The H_2SO_4 concentration as the acceptor (0.01 M H_2SO_4);
3. The H_2SO_4 concentration as the carrier (3 M H_2SO_4 was chosen);
4. The temperature in the 20–60 ºC interval (exponential increase of sensitivity).

The major interferent of this method are Br^- anions, because they can be oxidized on-line by permanganate to form molecular species which are reducible at the platinum electrode at the applied potential. The iodate pre-treatment method was used to expel Br$^-$ out of solution. The water samples from the power plant contained small amounts of hydrazine which were expelled by treatment with bromate.

The reproducibility of the analytical system was analysed by five repetitive injections of chloride standard. The relative standard deviation for a 2 mM Cl$^-$ standard was 0.61 % and for a 5 μM it was 1.11 %. The detection limit at room temperature was 0.05 μM Cl$^-$ which corresponded to 35.5 pg of Cl$^-$. The sample loop volume was 0.200 ml. The throughput of this method is 60 samples per hour.

The method is successfully applied for the determination of chloride (without concentrating or diluting the samples) in seawater, tap water, mineral waters ("Minakva") and water from the water-steam system of the power plant "Nikola Tesla B" in Obrenovac.

ИЗВОД

ОПТИМИЗАЦИЈА И ПРИМЕНА ГАСНО-ДИФУЗИОНЕ ПРОТОЧНЕ ИНЈЕКЦИОНЕ МЕТОДЕ ЗА ОДРЕЂИВАЊЕ ХЛОРИДА

АЛЕКСАНДАР ЛОЛИЋ, СНЕЖАНА НИКОЛИЋ-МАНДИЋ и ПРЕДРАГ ПОЛИЋ

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Селективан и осетљив поступак за брзо, индиректно одређивање хлорида гасно-дифузионом методом отпимизован је и примењен за одређивање хлорида у узорцима вода са врло различитим садржајем ове врсте: морској, води за пиће и врло чистим водама у систему вода-пара ТЕ "Никола Тесна Б" у Обреновцу. Употреба амперометријског детектора типа LC-17A омогућава снижавање границе детекције на 0.05 μmol/dm^3 хлорида (што за узорак запремине 0.2 cm^3 износи 35.5 pg) и подешавање брзине и смера тока у гасно-дифузионој јединици. Овако оптимизован проточни систем има одличну репродуктивност. За хлоридни стандард концентрације 5 μmol/dm^3 релативна стандардна девијација износи 1.11 % (*n* = 5).

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